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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery of large capacity, excellent in shelf life and cycle characteristics.

SOLUTION: The nonaqueous electrolyte secondary battery comprises at least a negative electrode and a positive electrode comprising carbonaceous material capable of occluding/releasing lithium, and an electrolyte in which lithium salt is dissolved in a nonaqueous solvent. Related to the negative electrode, a nucle material is a carbon material in which d002 value at X-ray diffraction is 0.335-0.338 nm. A carbonaceous material whose d002 value is larger than the nucle material sticks to a part of or the entire surface of the nucle material. A weight ratio between the nucle material and the carbonaceous material whose d002 value is larger than that is 99/1 to 80/20. The nonaqueous solvent contains at least one kind of vinylene carbonate compound and vinyl ethylene carbonate compound, respectively.

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CLAIMS

[Claim(s)]

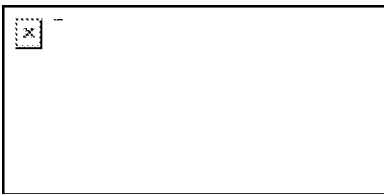
[Claim 1] In the nonaqueous electrolyte rechargeable battery which consists of a negative electrode which consists a lithium of occlusion and a carbonaceous ingredient which can be emitted, a positive electrode, and the electrolytic solution which comes to dissolve lithium salt in a non-aqueous solvent at least A negative electrode uses as karyomitome the carbon material whose d value of the lattice plane (002nd page) in an X diffraction is 0.335-0.338nm. The carbonaceous object with large d value of a part of front face of the karyomitome or a lattice plane [in / all are boiled and / from said karyomitome / an X diffraction] (002nd page) has adhered. And a carbonaceous object with larger d value of the lattice plane (002nd page) in an X diffraction than karyomitome and said karyomitome is the rate of 99 / 1 - 80/20 in a weight ratio. Furthermore, the nonaqueous electrolyte rechargeable battery characterized by containing at least the vinyl ethylene carbonate compound expressed with the vinylene carbonate compound expressed with the following general formula (I) in said non-aqueous solvent, and the following general formula (II) a kind every.

[Formula 1]



(R1 and R2 express independently a hydrogen atom or the alkyl group of carbon numbers 1-4 among a formula, respectively.)

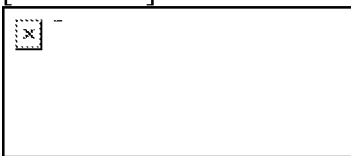
[Formula 2]



(R3, R4, and R5 express independently a hydrogen atom or the alkyl group of carbon numbers 1-4 among a formula, respectively, and R6, R7, and R8 express independently a hydrogen atom, the alkyl group of carbon numbers 1-4, or the alkenyl radical of carbon numbers 2-7, respectively.)

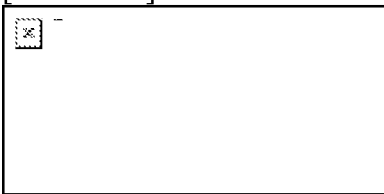
[Claim 2] The carbon material whose d value of the lattice plane (002nd page) in an X diffraction is 0.335-0.338nm is used as karyomitome. The carbonaceous object with large d value of a part of front face of the karyomitome or a lattice plane [in / all are boiled and / from said karyomitome / an X diffraction] (002nd page) has adhered. The lithium with which 99 / 1 - 80/20 come out comparatively by the weight ratio, and a carbonaceous object with larger d value of the lattice plane (002nd page) in an X diffraction than karyomitome and said karyomitome contains a certain carbonaceous ingredient And occlusion and the negative electrode which can be emitted, It is the nonaqueous electrolyte for nonaqueous electrolyte rechargeable batteries equipped with the positive electrode at least. This nonaqueous electrolyte consists of a non-aqueous solvent and lithium salt at least. The nonaqueous electrolyte characterized by containing at least the vinyl ethylene carbonate compound expressed with the vinylene carbonate compound expressed with the following general formula (I) in said non-aqueous solvent, and the following general formula (II) a kind every.

[Formula 3]



(R1 and R2 express independently a hydrogen atom or the alkyl group of carbon numbers 1-4 among a formula, respectively.)

[Formula 4]



(R3, R4, and R5 express independently a hydrogen atom or the alkyl group of carbon numbers 1-4 among a formula, respectively, and R6, R7, and R8 express independently a hydrogen atom, the alkyl group of carbon numbers 1-4, or the alkenyl radical of carbon numbers 2-7, respectively.)

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a nonaqueous electrolyte rechargeable battery. According to this invention, offer of the nonaqueous electrolyte rechargeable battery which was excellent in the preservation property and the cycle property with high capacity is attained by using the nonaqueous electrolyte by which the specific negative electrode and the compound of specific structure were added.

[0002]

[Description of the Prior Art] Development of a lithium secondary battery with a high energy density is furthered with lightweight-izing of an electric product in recent years, and a miniaturization. Moreover, the improvement of a cell property is also demanded with expansion of Field of application of a lithium secondary battery. Research is briskly done for many years as a cell by which the rechargeable battery which uses a metal lithium as a negative electrode can attain high capacity-ization. However, a metal lithium grows in the shape of a dendrite by the repeat of charge and discharge, finally reaches a positive electrode and has the problem that a short circuit will arise in the interior of a cell. This problem is the biggest technical technical problem at the time of putting a metal lithium secondary battery in practical use.

[0003] To this, the nonaqueous electrolyte rechargeable battery which used occlusion and the carbonaceous ingredient which can be emitted is proposed in lithiums, such as corks, an artificial graphite, and a natural graphite, by the negative electrode. In such a nonaqueous electrolyte rechargeable battery, since a lithium does not exist in the state of a metal, formation of a dendrite is controlled, and a battery life and safety can be improved. Especially the nonaqueous electrolyte rechargeable battery using graphite system carbonaceous ingredients, such as an artificial graphite and a natural graphite, attracts attention as what meets the demand of high-capacity-izing.

[0004] In the lithium secondary battery which uses the above-mentioned carbonaceous ingredient, annular carbonate, such as propylene carbonate and ethylene carbonate, is usually widely used as a high dielectric constant solvent of a nonaqueous electrolyte. In the nonaqueous electrolyte rechargeable battery using non-graphite system carbonaceous ingredients, such as corks, the solvent containing propylene carbonate can use suitably. On the other hand, in the nonaqueous electrolyte rechargeable battery which is independent, or mixed the graphite system carbonaceous ingredient with other negative-electrode material which can emit [occlusion and] a lithium, and was used as the negative electrode, if the solvent containing propylene carbonate is used, the decomposition reaction of propylene carbonate will advance violently in an electrode surface at the time of charge, and the occlusion and emission of the smooth lithium to a graphite system carbonaceous negative electrode will become impossible.

[0005] On the other hand, since there is little such decomposition, as the electrolytic solution of the nonaqueous electrolyte rechargeable battery using a graphite system carbonaceous negative electrode, as for ethylene carbonate, ethylene carbonate is used abundantly as a high dielectric constant solvent. However, in order that the electrolytic solution might decompose [in / as a main solvent / a charge-and-discharge process]

ethylene carbonate in an electrode surface, there were problems, such as decline in charge-and-discharge effectiveness, a fall of a cycle property, and a rise of the cell internal pressure by the generation of gas.

[0006] Then, using combining a crystalline low carbonaceous ingredient rather than a graphite with low decomposition activity is proposed as the graphite system carbonaceous ingredient to the electrolytic solution. For example, it covers with the organic substance which can carbonize graphite system carbonaceous, and the amorphous covering graphite system carbon matter carbonized by calcinating the covering object is manufactured and used. As for this carbon matter, the further amelioration is desired although effectiveness is looked at by decomposition control of the electrolytic solution.

[0007] About the electrolytic solution, various additives are proposed for the improvement in a property of a nonaqueous electrolyte rechargeable battery. In order to control disassembly of the electrolytic solution of the nonaqueous electrolyte rechargeable battery using a graphite system negative electrode, the electrolytic solution (JP,2000-40526,A) which contains in the electrolytic solution (JP,8-45545,A) containing vinylene carbonate and its derivative or a side chain the ethylene carbonate derivative which has a disconjugation unsaturated bond is proposed. Reduction decomposition of said compound is carried out on a negative-electrode front face, the electrolytic solution containing these compounds forms a coat, and too much disassembly of the electrolytic solution is controlled by this coat. However, these compounds are necessarily unsatisfying about the preservation property under hot environments 80 degrees C or more. Moreover, the positive-electrode material of a charge condition tends to react, and a vinylene carbonate compound is in the inclination for a preservation property to fall, when an addition increases.

[0008]

[Problem(s) to be Solved by the Invention] This invention is made in view of said trouble, suppresses disassembly of the electrolytic solution of the nonaqueous electrolyte rechargeable battery using the negative electrode containing a carbonaceous ingredient to the minimum, and its charge-and-discharge effectiveness is high, and it offers the nonaqueous electrolyte rechargeable battery of the high energy consistency which excelled [bottom / of an elevated temperature] in the preservation property and the cycle property.

[0009]

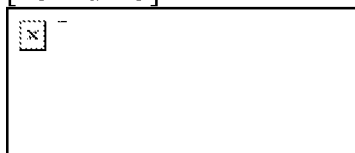
[Means for Solving the Problem] In order to attain the above-mentioned purpose, as a result of repeating various examination, this invention person etc. finds out that disassembly of the electrolytic solution can be suppressed to the minimum, charge-and-discharge effectiveness can be raised, and a preservation property and a cycle property can be raised by using the negative electrode which consists of a specific carbon material, and the specific electrolytic solution, and came to complete this invention.

[0010] The negative electrode which this invention is completed based on such knowledge, and consists a lithium of occlusion and a carbonaceous ingredient which can be emitted, In the nonaqueous electrolyte rechargeable battery which consists of a positive electrode and the electrolytic solution which comes to dissolve lithium salt in a non-aqueous solvent at least A negative electrode uses as karyomitome the carbon material whose d value of the lattice plane (002nd page) in an X diffraction is 0.335-0.338nm. The carbonaceous object with large d value of a part of front face of the karyomitome or a

lattice plane [in / all are boiled and / from said karyomitome / an X diffraction] (002nd page) has adhered. And a carbonaceous object with larger d value of the lattice plane (002nd page) in an X diffraction than karyomitome and said karyomitome is the rate of 99 / 1 - 80/20 in a weight ratio. Furthermore, the vinyl ethylene carbonate compound expressed with the vinylene carbonate compound expressed with the following general formula (I) in said non-aqueous solvent and the following general formula (II) is characterized by containing a kind every at least.

[0011]

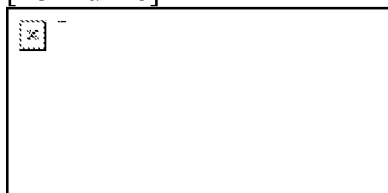
[Formula 5]



[0012] (R1 and R2 express independently a hydrogen atom or the alkyl group of carbon numbers 1-4 among a formula, respectively.)

[0013]

[Formula 6]



[0014] (R3, R4, and R5 express independently a hydrogen atom or the alkyl group of carbon numbers 1-4 among a formula, respectively, and R6, R7, and R8 express independently a hydrogen atom, the alkyl group of carbon numbers 1-4, or the alkenyl radical of carbon numbers 2-7, respectively.)

Moreover, this invention uses as karyomitome the carbon material whose d value of the lattice plane (002nd page) in an X diffraction is 0.335-0.338nm. The carbonaceous object with large d value of a part of front face of the karyomitome or a lattice plane [in / all are boiled and / from said karyomitome / an X diffraction] (002nd page) has adhered. The lithium with which 99 / 1 - 80/20 come out comparatively by the weight ratio, and a carbonaceous object with larger d value of the lattice plane (002nd page) in an X diffraction than karyomitome and said karyomitome contains a certain carbonaceous ingredient And occlusion and the negative electrode which can be emitted, It is the nonaqueous electrolyte for nonaqueous electrolyte rechargeable batteries equipped with the positive electrode at least. This nonaqueous electrolyte consists of a non-aqueous solvent and lithium salt at least. The vinyl ethylene carbonate compound expressed with the vinylene carbonate compound expressed with the following general formula (I) in said non-aqueous solvent and the following general formula (II) is characterized by containing a kind every at least.

[0015]

[Formula 7]



[0016] (R1 and R2 express independently a hydrogen atom or the alkyl group of carbon numbers 1-4 among a formula, respectively.)

[0017]

[Formula 8]



[0018] (R3, R4, and R5 express independently a hydrogen atom or the alkyl group of carbon numbers 1-4 among a formula, respectively, and R6, R7, and R8 express independently a hydrogen atom, the alkyl group of carbon numbers 1-4, or the alkenyl radical of carbon numbers 2-7, respectively.)

In the rechargeable battery whose offer is attained in this invention From the time of early charge, the compound coat of the reduction resultant of the vinylene carbonate compound origin and the reduction resultant of the vinyl ethylene carbonate compound origin generates efficiently to the part where the electrolytic-solution decomposition activity on said front face of a negative electrode is high. Although it is not clear, since the reduction resultants of a vinylene carbonate compound and a vinyl ethylene carbonate compound differ, the compound coat of a reason is stable also under hot environments, and he controls disassembly of too much electrolytic solution, and it is thought that charge-and-discharge effectiveness, a preservation property, and a cycle property are raised.

[0019]

[Embodiment of the Invention] The negative electrode which this invention is completed based on such knowledge, and consists a lithium of occlusion and a carbonaceous ingredient which can be emitted, In the nonaqueous electrolyte rechargeable battery which consists of a positive electrode and the electrolytic solution which comes to dissolve lithium salt in a non-aqueous solvent at least A negative electrode uses as karyomitome the carbon material whose d value of the lattice plane (002nd page) in an X diffraction is 0.335-0.338nm. The carbonaceous object with large d value of a part of front face of the karyomitome or a lattice plane [in / all are boiled and / from said karyomitome / an X diffraction] (002nd page) has adhered. And a carbonaceous object with larger d value of the lattice plane (002nd page) in an X diffraction than karyomitome and said karyomitome is the rate of 99 / 1 - 80/20 in a weight ratio. Furthermore, the vinyl ethylene carbonate compound expressed with the vinylene carbonate compound expressed with a general formula (I) in said non-aqueous solvent and a general formula (II) is characterized by containing a kind every at least.

[0020] The artificial graphite with which the carbon material of a graphite system was manufactured as a carbon material used as karyomitome by elevated-temperature heat

treatment of the easy graphite pitch obtained from various raw materials preferably, for example, suitably, a natural graphite, the purification natural graphite which high-grade-ized this, or kish graphite is mainly used. As for d value (distance between layers) of the lattice plane (002nd page) which asked for these carbon materials by the X diffraction by Gakushin method, it is desirable that it is 0.335-0.338nm and is 0.335-0.337nm. It is desirable that it is 1 or less % of the weight, as for ash content, it is more desirable that it is 0.5 or less % of the weight, and it is desirable that it is especially 0.1 or less % of the weight. Moreover, it is desirable that it is 30nm or more, as for the microcrystal size (Lc) for which it asked by the X diffraction by Gakushin method, it is more desirable that it is 50nm or more, and it is desirable that it is especially 100nm or more.

[0021] Moreover, it is more desirable that it is 3-50 micrometers, it is desirable that it is 1-100 micrometers, and it is [as for the median size of the carbon material fine particles by the method of laser diffracting / being scattered about, it is still more desirable that it is 5-40 micrometers, and] desirable [a median size] that it is especially 7-30 micrometers. It is more desirable that it is 0.5-20.0m²/g, it is desirable that they are 0.3-25.0m² / g, and it is [as for BET adsorption method specific surface area, it is still more desirable that they are 0.7-15.0m² / g, and] desirable that they are especially 0.8-10.0m² / g. Moreover, when [in used Ar-ion-laser light for the fine particles adjusted to said path] Raman spectrum analysis is carried out, Intensity ratio R=IB of the peak PA of the range of 1570-1620cm⁻¹, and (peak intensity IA) the peak PB (peak intensity IB) of the range of 1300-1400cm⁻¹ / IA 0.01-0.5 are desirable. As for especially the full width at half maximum of the range of 1570-1620cm⁻¹, it is [one or less / 26cm⁻¹ -] desirable that it is one or less [25cm⁻¹ -].

[0022] About the carbonaceous object adhering to the front face of this karyomitome where d value of the lattice plane (002nd page) in an X diffraction is larger than the carbon material used as karyomitome, although it will not be limited especially if crystallinity is lower than the carbon material used as karyomitome, that to which d value (distance between layers) of the lattice plane (002nd page) for which it asked by the X diffraction by Gakushin method exceeds 0.338nm is desirable. Usually, as for d value, the thing to about 0.36nm is used.

[0023] a carbonaceous object with larger d value of the lattice plane (002nd page) in an X diffraction than karyomitome and said karyomitome -- comparatively (karyomitome / surface carbonaceous object) -- ***** -- it is desirable from improvement in energy density, and the point of a cycle property 99 / 1 - 80/20, and to be preferably referred to as 99 / 1 - 85/15 by the weight ratio. Although not limited especially about the gestalt of a carbonaceous object with larger d value of the lattice plane (002nd page) in an X diffraction than karyomitome and said karyomitome, the "polyphase structure graphite system carbonaceous object" which is the gestalt which the carbonaceous object with larger d value of the lattice plane (002nd page) in an X diffraction than said karyomitome adhered or covered to surface some or surface all of a karyomitome particle is desirable.

[0024] The above-mentioned polyphase structure graphite system carbonaceous object can mix and calcinate a graphite system carbon material with the organic substance etc., or can make amorphous carbon form in a front face using a CVD method etc. As the organic substance, petroleum system heavy oil, such as ethylene tar division-into-equal-parts solution system heavy oil which carries out a byproduction, is mentioned at the time of pyrolyses, such as straight run system heavy oil, such as coal system heavy oil, such as

a coal-tar pitch from a soft pitch to a hard pitch, and a pyrolysis oil, and ordinary pressure residual oil, reduced pressure residual oil, a crude oil, and naphtha. Moreover, what was ground to 1 micrometer - 100 micrometers can use the solid-state-like residue object which distilled these heavy oil at 200 degrees C - 400 degrees C, and was obtained.

Furthermore, vinyl chloride resin, phenol resin, and imide resin are also used.

[0025] Mixing with a graphite system carbon material and the organic substance can use further the V type mixer which used the moving vane and which stirs, and can use kneading type mixing equipments, such as a formula mixer, a kneader, a paddle form kneading machine, and a roll form kneading machine, and is mixed by rotation of the container itself, a cylindrical shape mixer, a double cone mixer, the ribbon mixer using a mixed wing, the paddle dryer using a rotation paddle, etc.

[0026] In this way, the polyphase structure graphite system carbonaceous object which is the carbonaceous ingredient which the mixture of the graphite system carbon material and the organic substance which were obtained was calcinated [ingredient] in the inert gas ambient atmosphere, and made amorphous carbon form in a front face can be obtained. Nitrogen, an argon, etc. can be used as inert gas. Moreover, as a burning temperature, the range of 400-2000 degrees C is desirable, and, in addition, the range which is 700-1500 degrees C is desirable.

[0027] The polyphase structure graphite system carbonaceous object after baking processes grinding, a crack, a classification, etc. with a suitable means, and is good also as fine particles, it is desirable that it is 1-100 micrometers, and it is [it is more desirable that it is 3-50 micrometers, and / as for the median size of fine particles according to the method of laser diffracting / being scattered about in that case, it is still more desirable that it is 5-40 micrometers and] desirable [median size] that it is especially 7-30 micrometers. It is more desirable that they are 0.5-20.0m² / g, it is desirable that they are 0.3-25.0m² / g, and it is [as for BET adsorption method specific surface area, it is still more desirable that they are 0.7-15.0m² / g, and] desirable that they are especially 0.8-10.0m² / g. moreover, the case which used Ar-ion-laser light for the fine particles adjusted to said path where Raman spectrum analysis is carried out -- intensity ratio R=IB of the peak PA of the range of 1570-1620cm⁻¹, and (peak intensity IA) the peak PB (peak intensity IB) of the range of 1300-1400cm⁻¹ / IA 0.1-1.2 are desirable and, as for the full width at half maximum of the range of 1570-1620cm⁻¹, it is desirable that it is 25-45cm⁻¹.

[0028] It can mix in the polyphase structure graphite system carbonaceous object obtained by the graphite system carbon material or the above used as the aforementioned nucleus further, and the negative-electrode material which can emit [occlusion and] other lithiums can also be used for it. As negative-electrode material which can emit [occlusion and] other lithiums, metal silicides, such as a lithium alloy of metallic sulfide ingredients, such as metallic-oxide ingredients, such as tin oxide and oxidization silicon, and sulfuration tin, a lithium metal, a lithium, and various metals, such as aluminum, silicon, tin, and antimony, and silicification magnesium, and silicification copper, can be illustrated. Two or more kinds may be mixed and these negative-electrode ingredients may be used.

[0029] It is not limited especially about the method of manufacturing a negative electrode using these negative-electrode ingredients. For example, it can apply to the substrate of a charge collector, and by drying, a negative electrode can be manufactured and roll

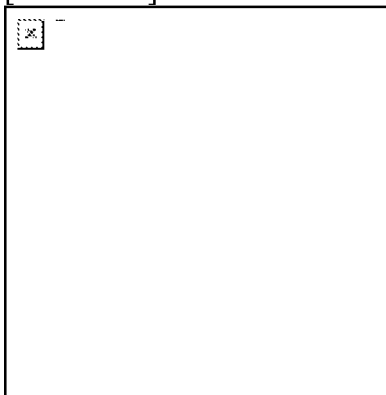
forming of this negative-electrode ingredient is carried out as it is, and a binder, a thickener, electric conduction material, a solvent, etc. can be added to a negative-electrode ingredient if needed, and it can consider as the shape of a slurry, and can also consider [it can consider as a sheet electrode or] as a pellet electrode with compression molding.

[0030] About the binder used for manufacture of an electrode, to the solvent or the electrolytic solution which are used at the time of electrode manufacture, if it is a stable ingredient, it will not be limited especially. As the example, polyvinylidene fluoride, polytetrafluoroethylene, styrene-butadiene rubber, polyisoprene rubber, butadiene rubber, etc. can be mentioned. As a thickener, carboxyl methyl cellulose, methyl cellulose, a hydroxymethyl cellulose, ethyl cellulose, polyvinyl alcohol, oxidization starch, phosphorylation starch, GAZEIN, etc. are mentioned.

[0031] As electric conduction material, carbon materials, such as metallic materials, such as copper and nickel, graphite, carbon black, and a carbon fiber, are mentioned. The quality of the material of the charge collector for negative electrodes has the point of metals, such as copper, nickel, and stainless steel, being used and being easy to process it into a thin film in these, and the point of cost to desirable copper foil. The non-aqueous solvent used for this invention contains the vinyl ethylene carbonate compound expressed with the vinylene carbonate compound expressed with the following general formula (I), and the following general formula (II).

[0032]

[Formula 9]



[0033] It sets to a general formula (I) and is R1 and R2. A hydrogen atom or the alkyl group of carbon numbers 1-4 is expressed independently, respectively. R1 and R2 When it is the alkyl group of carbon numbers 1-4, as the example, a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, sec-butyl, and tert-butyl are mentioned. A methyl group and an ethyl group are desirable in these.

[0034] And as an example of a vinylene carbonate compound expressed with such a general formula (I), vinylene carbonate, methyl vinylene carbonate, ethyl vinylene carbonate, 4, 5-dimethyl vinylene carbonate, 4, and 5-diethyl vinylene carbonate etc. can be mentioned. Especially, vinylene carbonate, 4, and 5-dimethyl vinylene carbonate is desirable, and especially vinylene carbonate is desirable. Two or more sorts may be mixed and these may be used.

[0035] It sets to a general formula (II) and is R3 and R4. And R5 A hydrogen atom or the alkyl group of carbon numbers 1-4 is expressed, and it is R6 and R7 independently,

respectively. And R8 A hydrogen atom, the alkyl group of carbon numbers 1-4, or the alkenyl radical of carbon numbers 2-7 is expressed independently, respectively. R3, R4, R5, R6, and R7 And R8 When it is the alkyl group of carbon numbers 1-4, as the example, a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, sec-butyl, and tert-butyl are mentioned. A methyl group and an ethyl group are desirable in these.

[0036] Moreover, R6 and R7 And R8 When it is the alkenyl radical of carbon numbers 2-7, as the example, a vinyl group, 1-methylvinyl radical, 2-methylvinyl radical, a propenyl radical, 1-methyl propenyl radical, 2-methyl propenyl radical, 3-methyl propenyl radical, a butenyl group, etc. are mentioned. And as an example of a vinyl ethylene carbonate compound expressed with such a general formula (II), 4-vinyl ethylene carbonate, 4-methyl-4-vinyl ethylene carbonate, 4-ethyl-4-vinyl ethylene carbonate, 4-n-propyl-4-vinyl ethylene carbonate, 5-methyl-4-vinyl ethylene carbonate, 4, and 4-divinyl ethylene carbonate, 4, and 5-divinyl ethylene carbonate etc. can be mentioned.

[0037] Especially, 4-vinyl ethylene carbonate, 4-methyl-4-vinyl ethylene carbonate, 4, and 5-divinyl ethylene carbonate is desirable, and especially 4-vinyl ethylene carbonate is desirable. Two or more sorts may be mixed and these may be used. In this invention, the content of the vinylene carbonate compound expressed with the general formula in a non-aqueous solvent (I) has 0.05 - 5 desirable % of the weight, and especially its 0.1 - 4 % of the weight is desirable. The content of the vinyl ethylene carbonate compound expressed with a general formula (II) has 0.05 - 5 desirable % of the weight, and especially its 0.1 - 4 % of the weight is desirable. In this invention, the total quantity of the compound expressed with the above-mentioned general formula (I) and a general formula (II) is usually 0.2 - 5 % of the weight preferably 0.1 to 6% of the weight.

[0038] It is not limited especially in the non-aqueous solvent used for this invention. For example, ethylene carbonate, Annular carbonate, such as propylene carbonate and butylene carbonate, Dimethyl carbonate, diethyl carbonate, G n-propyl carbonate, Dialkyl (thing of carbon numbers 1-4 is desirable) carbonate, such as ethyl methyl carbonate, Cyclic ether, such as a tetrahydrofuran and 2-methyl tetrahydrofuran, The chain-like ether, such as dimethoxyethane and dimethoxymethane, gamma-butyrolactone, Phosphorus-containing organic solvents, such as sulfur-containing organic solvents, such as chain-like ester, such as cyclic ester, such as gamma-valerolactone, methyl acetate, and ethyl propionate, sulfolane, and diethyl sulfone, trimethyl phosphate, and phosphoric-acid triethyl, etc. are mentioned. Two or more kinds may be mixed and these solvents may be used.

[0039] That whose non-aqueous solvent is a mixed solvent with which the chain-like carbonate chosen from the group which the carbon number of an alkylene group becomes from the annular carbonate chosen from the group which consists of alkylene carbonate of 2-4, and the dialkyl carbonate whose carbon numbers of an alkyl group are 1-4 is contained more than 20 capacity %, respectively, and these carbonate occupies more than the whole 70 capacity % here has the high conductivity of the electrolytic solution, and a cycle property and its high current discharge property are highly desirable.

[0040] The carbon number of an alkylene group can mention ethylene carbonate, propylene carbonate, butylene carbonate, etc. as an example of the alkylene carbonate of 2-4, for example, and ethylene carbonate and propylene carbonate are desirable in these. As an example of the dialkyl carbonate which is 1-4, the carbon number of an alkyl group

can mention dimethyl carbonate, diethyl carbonate, G n-propyl carbonate, ethyl methyl carbonate, methyl-n-propyl carbonate, ethyl-n-propyl carbonate, etc. Dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate are desirable in these. In addition, solvents other than carbonate may be contained in a mixed non-aqueous solvent.

[0041] As a mode of the non-aqueous solvent of other desirable electrolytic solutions, the own boiling point of a solvent of what contains especially one sort or two sorts or more of with a specific inductive capacity of 25 or more solvents at a rate more than 85 capacity % more than 60 capacity % is comparatively high, and, as for the problem of volatilization or a liquid spill, it is desirable few also in hot use. Moreover, what ethylene carbonate, propylene carbonate, gamma-butyrolactone, and gamma-valerolactone are mentioned as a with a specific inductive capacity of 25 or more non-aqueous solvent, and contains especially ethylene carbonate is desirable, the mixed solvent which occupies more than 5 capacity % and gamma-butyrolactone for ethylene carbonate more than 55 capacity % also in it, and the solvent which occupies more than 30 capacity % and propylene carbonate for ethylene carbonate more than 30 capacity % have little generation of gas at the time of elevated-temperature preservation, and the balance of a cycle property, a high current discharge property, etc. has it. [still more desirable well]

[0042] Although it is originally easy to decompose propylene carbonate, gamma-butyrolactone, etc. on a graphite front face when a graphite system carbon negative electrode is used, decomposition can be controlled by forming a stable coat in a graphite system carbon front face to the minimum by making a vinylene carbonate compound and a vinyl ethylene carbonate compound contain a kind every at least.

[0043] To a non-aqueous solvent, when the compound chosen from the group which consists of nitrogen-containing compounds, such as carboxylic anhydrides, such as sulfonates, such as ape fights, such as an ethylene ape fight, and a propane sultone, a succinic anhydride, a maleic anhydride, and phthalic anhydride, 1-methyl-2-pyrrolidinone, 1-methyl-2-piperidone, 3-methyl-2-oxazolidinone, 1,3-dimethyl-2-imidazolidinone, and N-methyl succinimide, is added so that it may become a non-aqueous solvent with 0.01 - 3 % of the weight, it is still more desirable at the point whose cycle property improves.

[0044] Furthermore, to a nonaqueous electrolyte, in order [with a separator or electrode material] to be smeared and to improve a sex, a surfactant may be added so that it may become a non-aqueous solvent with 0.01 - 2 % of the weight. Lithium salt is used as a solute of the electrolytic solution used by this invention. Although especially limitation will not be carried out if it can be used as a solute about lithium salt, as the example for example LiClO_4 , LiPF_6 , and LiBF_4 from -- the inorganic lithium salt or LiCF_3SO_3 chosen -- $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$, and $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ etc. -- fluorine-containing organic lithium salt is mentioned. The inside of these, and LiPF_6 and LiBF_4 It is desirable. In addition, two or more kinds may be mixed and these solutes may be used.

[0045] As for the lithium salt mol concentration of the solute in the electrolytic solution, it is desirable that it is 0.5-3 mols/l. When exceeding 1. in less than 0.5 mols [1.] /or three mols /, since the conductivity of the electrolytic solution falls and the engine performance of a cell falls, it is not desirable. Although it is not restricted but a well-known ingredient can be used especially as an ingredient of the positive electrode which constitutes the cell of this invention, the desirable ingredient which emits [occlusion and] lithiums, such as

lithium transition-metals multiple oxide ingredients, such as lithium cobalt oxide, a lithium nickel oxide, and a lithium manganic acid ghost, can be used.

[0046] Especially about the manufacture approach of a positive electrode, it is not limited but can manufacture according to the manufacture approach of the above-mentioned negative electrode. Moreover, about the configuration, after mixing, a well-known binder, electric conduction material, a solvent, etc. can be added to a positive-electrode ingredient if needed, and it applies to the substrate of a charge collector, and it can consider as a sheet electrode or can consider [press forming can be performed and] as a pellet electrode. As for the quality of the material of the charge collector for positive electrodes, metals, such as aluminum, titanium, and a tantalum, or the alloy of those is used. In these, since especially aluminum or its alloy is lightweight, it is desirable in respect of energy density.

[0047] It is not limited especially about the quality of the material or the configuration of a separator which are preferably used for the cell of this invention. However, it is stable to the electrolytic solution, and choosing from the solution retention outstanding ingredients is desirable, and it is desirable to use a porous sheet or a nonwoven fabric etc. which uses polyolefines, such as polyethylene and polypropylene, as a raw material. Especially about the method of manufacturing the cell of this invention which has a negative electrode, a positive electrode, and a nonaqueous electrolyte at least, it is not limited but can choose suitably from the approaches usually adopted.

[0048] Moreover, the coin type which carried out the laminating of the cylinder type, pellet electrode, and separator of the inside-out configuration which combined the cylinder type, pellet electrode, and separator which were not limited especially about the configuration of a cell but made the sheet electrode and the separator the shape of a spiral is usable.

[0049]

[Example] Although an example and the example of a comparison are given to below and this invention is explained to it still more concretely, this invention is not limited to these examples, unless the summary is exceeded.

d value of the lattice plane (002nd page) in an X diffraction 0.336nm, (Example 1) 100nm or more (652nm) and ash content 0.07 % of the weight, [crystallite size (Lc)] 12 micrometers and BET adsorption method specific surface area 7.5m² / g, [the median size by the method of laser diffracting / being scattered about] In the Raman spectrum analysis using Ar-ion-laser light The peak PA of the range of 1570-1620cm⁻¹ The full width at half maximum of the range of 0.12 and 1570-1620cm⁻¹ (Peak intensity IA) And 2kg of 19.9cm - natural-graphite powder which is 1 [intensity ratio R=IB of the peak PB (peak intensity IB) of the range of 1300-1400cm⁻¹ / IA] It mixed with petroleum system pitch 1kg, and the mixture of the shape of an acquired slurry was held at a temperature up and this temperature to 1100 degrees C under the inert atmosphere with the batch process heating furnace for 2 hours in 2 hours. This was ground, particle size was prepared to 18-22 micrometers with the oscillating-type sieve, and the "polyphase structure graphite system carbonaceous object" which finally covered the natural-graphite front face with 7% of amorphous carbon was obtained. d value of the lattice plane (002nd page) in the X diffraction of an amorphous carbon part was 0.345nm.

[0050] What mixed the polyvinylidene fluoride 6 weight section in the "polyphase structure graphite system carbonaceous object" 94 weight section, was made to distribute

by the N-methyl-2-pyrrolidone, and was made into the shape of a slurry by using a book "a polyphase structure graphite system carbonaceous object" as a negative-electrode active material was applied to homogeneity on copper foil with a thickness of 18 micrometers which is a negative-electrode charge collector, and after desiccation, it pierced to discoid with a diameter of 12.5mm, and considered as the negative electrode.

[0051] The carbon black 6 weight section and the polyvinylidene fluoride (Kureha chemistry company make, trade name:KF-1000) 9 weight section were added to the LiCoO₂ 85 weight section as positive active material, and it mixed, and distributed by the N-methyl-2-pyrrolidone, and what was made into the shape of a slurry was applied to homogeneity on aluminium foil with a thickness of 20 micrometers which is a positive-electrode charge collector, and after desiccation, it pierced to discoid with a diameter of 12.5mm, and considered as the positive electrode.

[0052] About the electrolytic solution, it adds into the mixture (3:7 capacity factors) of ethylene carbonate and ethyl methyl carbonate at a rate of 1 % of the weight of vinylene carbonate, and 1 % of the weight of vinyl ethylene carbonate, using as a solute LiPF₆ which fully dried under desiccation argon atmosphere, and is LiPF₆ further. It dissolved and prepared at a rate of one mol/l.

[0053] The positive electrode was held in the can made from stainless steel which serves as a positive-electrode charge collector using these positive electrodes, a negative electrode, and the electrolytic solution, and the negative electrode was laid through the separator which infiltrated the electrolytic solution on it. the obturation plate which serves both as this can and a negative-electrode conductor -- the gasket for an insulation - - minding -- it sealed in total and the coin mold cell was produced.

(Example 1 of a comparison) Vinylene carbonate is added at a rate 2% of the weight into the mixture (3:7 capacity factors) of ethylene carbonate and ethyl methyl carbonate, and it is LiPF₆ further. The coin mold cell was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0054] (Example 2 of a comparison) Vinyl ethylene carbonate is added at a rate 2% of the weight into the mixture (3:7 capacity factors) of ethylene carbonate and ethyl methyl carbonate, and it is LiPF₆ further. The coin mold cell was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0055] (Example 2) Vinylene carbonate is added into the mixture (1:9 capacity factors) of ethylene carbonate and gamma-butyrolactone at a rate of 1 % of the weight and 1 % of the weight of vinyl ethylene carbonate, and it is LiBF₄ further. It dissolved and prepared at a rate of two mols/l.

(Example 3 of a comparison) Vinylene carbonate is added at 2% of the weight of a rate into the mixture (1:9 capacity factors) of ethylene carbonate and gamma-butyrolactone, and it is LiBF₄ further. The coin mold cell was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of two mols/l.

[0056] (Example 4 of a comparison) Vinyl ethylene carbonate is added at 2% of the weight of a rate into the mixture (1:9 capacity factors) of ethylene carbonate and gamma-butyrolactone, and it is LiBF₄ further. The coin mold cell was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of two mols/l.

[0057] (Example 3) It adds into the mixture (5:5 capacity factors) of ethylene carbonate and propylene carbonate at a rate of 1 % of the weight of vinylene carbonate, and 1 % of

the weight of vinyl ethylene carbonate, and is LiPF₆ further. The coin mold cell was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0058] (Example 5 of a comparison) Vinylene carbonate is added at a rate 2% of the weight into the mixture (5:5 capacity factors) of ethylene carbonate and propylene carbonate, and it is LiPF₆ further. The coin mold cell was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0059] (Example 6 of a comparison) Vinyl ethylene carbonate is added at a rate 2% of the weight into the mixture (5:5 capacity factors) of ethylene carbonate and propylene carbonate, and it is LiPF₆ further. The coin mold cell was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0060] (Example 4) It adds at a rate of 1 % of the weight of vinylene carbonate, and 1 % of the weight of vinyl ethylene carbonate into the mixture (2:1:7 capacity factors) of ethylene carbonate, propylene carbonate, and gamma-butyrolactone, and is LiBF₄ further. The coin mold cell was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of 1.5 mols/l.

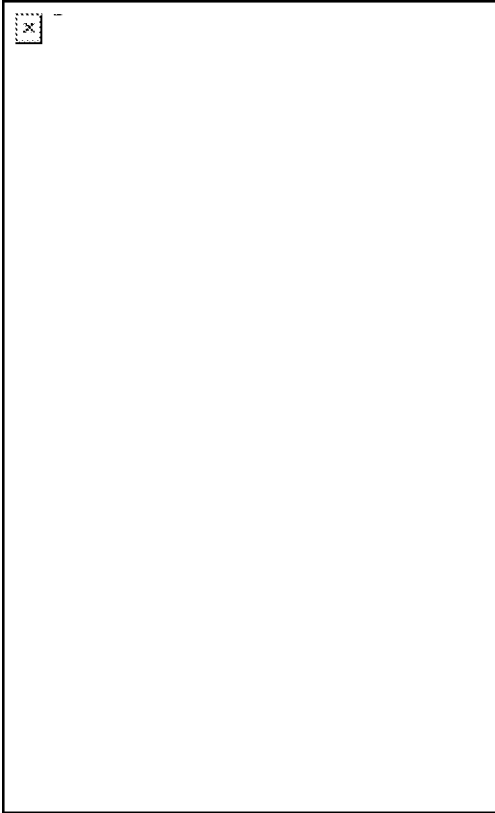
[0061] (Example 7 of a comparison) It adds at a rate of 2 % of the weight of vinylene carbonate into the mixture (2:1:7 capacity factors) of ethylene carbonate, propylene carbonate, and gamma-butyrolactone, and is LiBF₄ further. The coin mold cell was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of 1.5 mols/l.

[0062] (Example 8 of a comparison) It adds at a rate of 2 % of the weight of vinyl ethylene carbonate into the mixture (2:1:7 capacity factors) of ethylene carbonate, propylene carbonate, and gamma-butyrolactone, and is LiBF₄ further. The coin mold cell was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of 1.5 mols/l.

[0063] (Cell performance test) In 25 degrees C, the cell of these examples 1-4 and the examples 1-8 of a comparison was saved for three days at 85 degrees C in the state of charge, after 5 cycle lines are stabilized in charge termination electrical-potential-difference 4.2V in 0.5mA constant current and stabilized charge and discharge in discharge-final-voltage 3V. After making the cell after preservation discharge to discharge-final-voltage 3V by 0.5mA constant current in 25 degrees C, charge termination electrical-potential-difference 4.2V were performed by 0.5mA constant current, charge and discharge were performed by discharge-final-voltage 3V, and the preservation property was examined. The discharge capacity after the preservation at the time of setting discharge capacity before preservation to 100 is shown in Table 1.

[0064]

[Table 1]



[0065] The discharge capacity of the cell of this example after the preservation to the discharge capacity before preservation is improving, and effectiveness is in improvement in the preservation property in an elevated temperature so that clearly from Table 1.

[0066]

[Effect of the Invention] In the nonaqueous electrolyte rechargeable battery equipped with the negative electrode containing a carbonaceous ingredient, a negative electrode uses as karyomitome the carbon material whose d value of the lattice plane (002nd page) in an X diffraction is 0.335-0.338nm. The carbonaceous object with large d value of a part of front face of the karyomitome or a lattice plane [in / all are boiled and / from said karyomitome / an X diffraction] (002nd page) has adhered. And a carbonaceous object with larger d value of the lattice plane (002nd page) in an X diffraction than karyomitome and said karyomitome is the rate of 99 / 1 - 80/20 in a weight ratio. At least the vinyl ethylene carbonate compound expressed with the vinylene carbonate compound expressed with a general formula (I) in said non-aqueous solvent, and a general formula (II) a kind every furthermore, by containing While suppressing disassembly of the electrolytic solution to the minimum and obtaining a high capacity, the cell which was excellent in the preservation property and the cycle property under the elevated temperature can be produced, and it can contribute to the miniaturization of a nonaqueous electrolyte rechargeable battery, and high performance-ization.

[Translation done.]
